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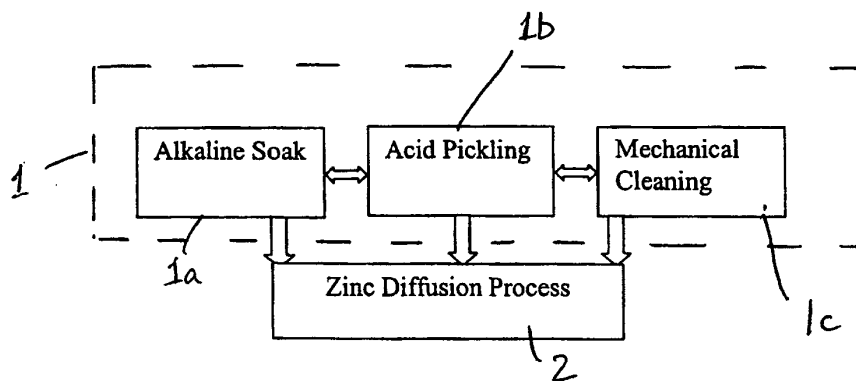
(56) Documents Cited
GB 0412989 A **GB 0261502 A**
EP 0834592 A1 **JP 2000160320 A**
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(54) Abstract Title
Reducing the corrosivity of magnesium containing alloys

(57) A magnesium containing metallic material comprises a surface layer in which zinc has been diffused. The material is preferably a magnesium alloy containing at least 85 weight % magnesium, up to 12 weight % aluminium, up to 2 weight % zinc and up to 0.5 weight % manganese. The surface layer may have a thickness of 1-7 μm , have a zinc concentration at least five times that of the interior of the material which is preferably at least 5 weight %. The layer may be produced by heating the material together with particles containing zinc at a temperature of 310-350°C for at least four hours. The particles may be substantially elemental zinc or they may be a zinc alloy (e.g. alloyed with aluminium or magnesium). The particles may be mixed with particles of an inert filler such as kaolin, calcium carbonate, magnesium carbonate, talc, alumina, silica or mica.

**FIGURE 1**DOCKETED
EIPD**13 JAN 2003****GB 2 376 693 A**

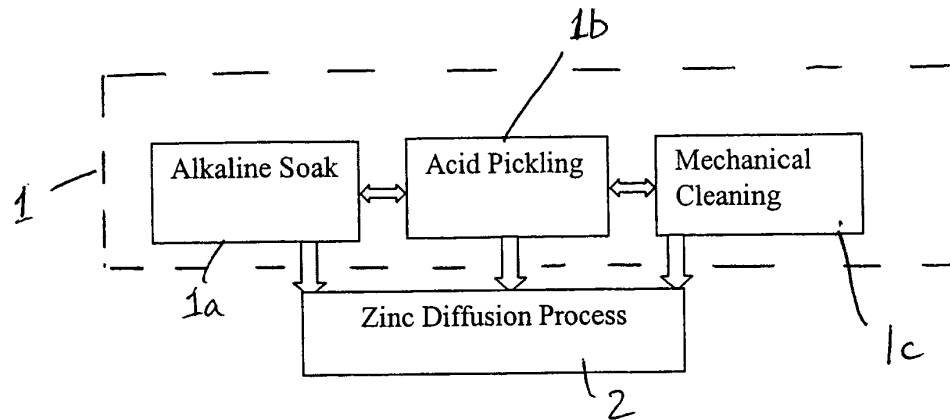


FIGURE 1

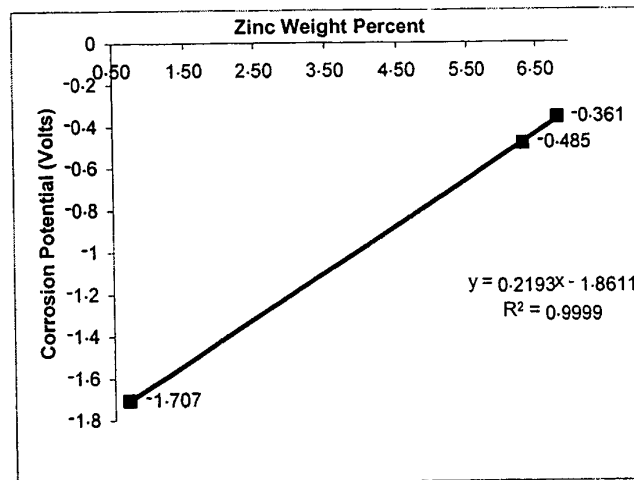
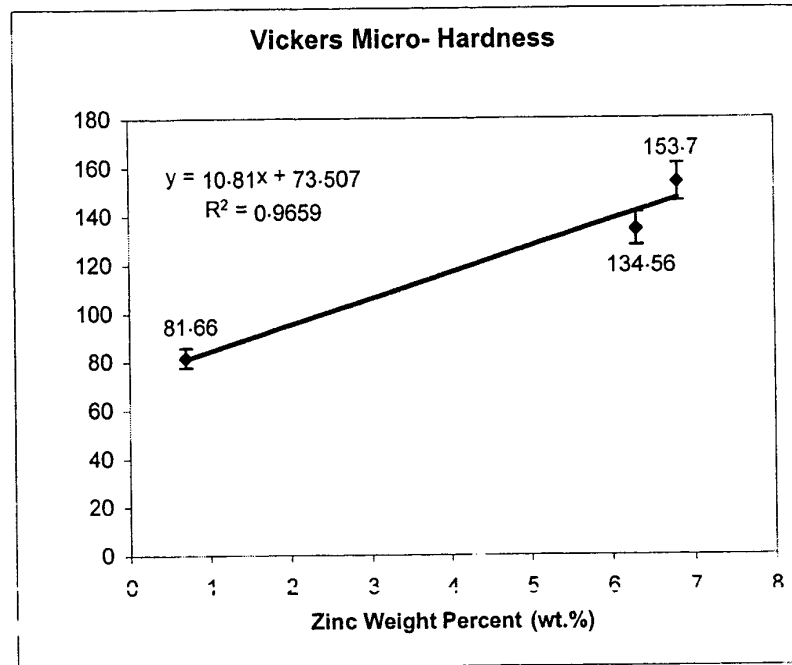


FIGURE 2

**Figure 3**

IMPROVED METALLIC MATERIALS AND THEIR PRODUCTION**Field of the Invention**

This invention relates to improved metallic materials and their production. In particular, it relates to improved magnesium containing materials such as magnesium alloys and a method of producing such materials.

Background of the Invention

In the electronics industry, especially in the audio, video, computer and communications (AVCC) sector, there is a constant drive to reduce the size and weight of products and to make them more easily portable. One of the ways in which this is achieved is to use suitably lightweight materials as constructional materials.

Magnesium has a density which is roughly two thirds that of aluminium and is only slightly higher than that of fibre reinforced plastics yet has excellent mechanical and physical properties as well as good processibility and recyclability. Its use as a constructional material in the electronics industries, especially the AVCC sector, and in other industries such the automotive industry, has been proposed and widely investigated.

Magnesium based materials potentially offer other benefits in the electronics industry, such as good shielding from electromagnetic interference (EMI) and good thermal conductivity which facilitates heat dissipation from components, e.g. when contained in a case made of the material. Thus, magnesium based materials are seen as attractive alternatives to

plastics materials for use as constuctional materials in the electronics and other industries, especially the AVCC sector.

However, magnesium has a high reactivity with other
5 substances which may be present in the environment in which the material is used. The corrosion potential of Mg alloys is known to be about -1.7 volts which gives rise to significant galvanic corrosion when such alloys come into contact with components made from other
10 metals, e.g. used as constructional or conducting components. This galvanic corrosivity is a major shortcoming of Mg alloys.

Various attempts have been made in the prior art to reduce the galvanic corrosivity of magnesium but none
15 has proved entirely satisfacory. For example, chromate coatings have been applied electrochemically. However, such coatings have inferior mechanical properties. Such coatings do not have good adhesion to the substrate layer and are easily removed by scratching or by
20 chemicals. Also, nickel protective coatings have been applied but again these coatings do not have a good adhesion and stability. Such coatings swell if subjected to a standard salt fog test. Further, anodising has been used as a coating treatment. However anodised coatings
25 are not electrically and thermally conducting.

The purpose of the present invention is to provide a magnesium based material, and a method of producing such a material, which has a reduced tendency to show galvanic corrosion but which retains suitable mechanical
30 and other properties such as conductivity which are

desirable for use in the electronics and other industries.

Summary of the Invention

According to the present invention in a first
5 aspect there is provided a metallic material which
comprises magnesium having a surface layer in which
zinc has been diffused into the material to provide
atomic substitution of the magnesium, the material
having a corrosion potential having a magnitude of
10 less than -0.6 volts.

Desirably, the corrosion potential of the metallic
material has a magnitude of less than -0.5 volts,
especially less than -0.4 volts. In this specification
corrosion potential is as measured against a standard
15 calomel electrode.

The metallic material according to the first aspect
of the invention may comprise a magnesium alloy, e.g.
containing at least 85%, in many cases at least 90%, in
some cases at least 95%, by weight magnesium. Other
20 elements present in such an alloy may include one or
more elements which do not substantially interfere with
the diffusion of zinc into the material, for example
aluminium, e.g. up to 12% by weight, such as 2% to 10%
by weight, zinc (already present in the base material),
25 e.g. up to 2% by weight, e.g. from 0.1% to 1% by
weight, and manganese, e.g. up to 0.5% by weight, e.g.
from 0.1% to 0.4% by weight.

The metallic material according to the first
aspect of the invention may have a surface layer having
30 a thickness of between $1\mu\text{m}$ and $7\mu\text{m}$, especially between
 $3\mu\text{m}$ and $5\mu\text{m}$, in which the concentration of zinc is

higher than in the interior of the material. The properties of the surface layer may be measured for example by EDS (energy dispersive spectroscopy), X-ray diffraction and micro-hardness or hardness. For
 5 example, the average concentration of zinc may be at least five times greater (measured on a percentage of alloy weight basis) in the said surface layer than in the interior of the metallic material. The average zinc concentration in the surface layer may be at least 5
 10 weight per cent, preferably at least 6 weight per cent, especially at least 6.5 weight per cent.

The metallic material according to the first aspect of the invention may suitably have the following properties:

- 15 (i) an electrical conductivity in its zinc diffused surface layer of at least 7 MS/m, e.g. from 7.3 MS/m to 10 MS/m or, for example an electrical volume resistivity in the range of 89 n ohm-m to 165 n ohm-m;
- 20 (ii) a Vickers micro-hardness of at least 100 kg/mm², e.g. at least 120 kg/mm², at 50 grams load.

The metallic material according to the first aspect of the invention may be in the form of a casting and/or it may have been prepared by any other metal forming hot
 25 or cold process, e.g. extrusion, forging, rolling etc. It may have been formed into the shape of an article before or after diffusion of zinc into the material. For example, the article shape may be that of a housing or case or chassis, e.g. for use in the automotive or
 30 electronics industry, especially in the AVCC sector.

According to the present invention in a second aspect there is provided a method of producing a metallic material according to the first aspect of the invention which comprises heating a metallic material
5 comprising magnesium together with zinc so that zinc diffuses into said material and produces a surface layer in which magnesium atoms are substituted by zinc.

In the method according to the second aspect of the invention the zinc employed is preferably elemental zinc
10 (e.g. containing not more than 2% by weight in total of other elements) although it may also be in the form of a suitable zinc alloy or compound, e.g. an inorganic or organic compound. Elemental zinc is preferred because less material is required than when the zinc is present
15 as an alloy or compound. Also, when the zinc is present as an alloy or compound, some energy is required to free the zinc before it can take part in the diffusion process.

Where the zinc is present as an alloy, the alloy
20 preferably contains at least 50% by weight of zinc. The other constituent(s) of the alloy is/are chosen so that the corrosion potential will not be made worse by the other constituent(s). The other constituent(s) should therefore be one or more elements other than copper,
25 iron and nickel. The content of copper, iron and nickel present as trace impurities (in the treated magnesium alloy and also in the zinc or zinc compound or alloy) preferably should not be greater than 150ppm Cu, 40ppm Fe and 10ppm Ni, where 'ppm' denotes parts per million
30 by weight. The other constituent(s) of a zinc alloy should also be chosen (i) to have a melting temperature less than 700°C, (ii) to provide an alloy with zinc

which does not contain intermetallic phases, (iii) to have a suitable diffusivity into magnesium, and (iv) to have a difference in atomic radius from that of Mg of not more than 15%. Suitable other constituents are
5 magnesium and/or aluminium.

In the method according to the second aspect of the invention the zinc employed (either elemental or in the form of a compound or alloy) preferably is in the form of particles or flakes, e.g. having a mean particle size
10 of less than 1000µm, especially less than 500µm.

The method according to the second aspect of the invention may be carried out at a temperature of from 250°C to 380°C, especially from 310°C to 350°C. The heating at this temperature may be carried out for a
15 period of at least 1 hour, preferably at least 4 hours, e.g. between 4 hours and 24 hours, especially from 12 hours to 18 hours.

The amount of zinc present to treat the metallic material in the method according to the first aspect of
20 the invention should be sufficient to cover the surface of the magnesium material to be treated to give uniform diffusion into the magnesium material. Typically, the amount by weight of zinc where present in elemental form to treat 1kg of magnesium may be from 6kg to 12kg. Any
25 unused zinc left after the method has been completed may be recycled and later re-used.

In the method according to the second aspect of the invention, an inert filler may be mixed with the zinc (in elemental, compound or alloy form) to
30 facilitate even distribution of the zinc and to prevent damage to the material being treated. The inert filler may form up to 30% by weight based on the weight of zinc

present. The inert filler may for example be an inorganic particulate material which does not react with the metallic material at the temperature(s) of the heating step. For example, the inert filler may be
5 selected from kaolin, calcium carbonate, magnesium carbonate, talc, alumina, silica, mica and the like. The inert filler may conveniently have a mean particle size of less than 200µm, e.g. less than 50µm.

The method according to the invention may be
10 carried out using a sealed container to contain the metallic material to be treated and the zinc plus any additive, e.g. inert filler. Such a container and its contents may be heated in a furnace or oven in an atmosphere of air or under one or more inert gases, e.g.
15 argon, helium, neon, krypton and the like, or a reducing gas atmosphere, e.g. using CO₂, SF₆, N₂ or the like, or a mixture of inert with reducing gas atmospheres at any relative concentrations. Slow rotation of the container may beneficially be applied. The furnace may be fixed
20 and the container rotated therein. Alternatively, the furnace may itself rotate, e.g. it may be a rotating barrel furnace.

In the method according to the second aspect, the metallic material to be treated may be in the form of a
25 body, e.g. a product which has been produced by a metal forming process such as casting or one of the other processes referred to earlier. Preferably, the body is provided in a shape having mainly flat surfaces to facilitate coverage of its surfaces with the zinc. It is
30 in some cases convenient for the body to be in the shape of an article for subsequent use.

The method according to the second aspect of the invention preferably includes, prior to the said heating, treatment of the metallic material to prepare and clean its surface. The treatment may include one or
5 more known treatments such as one or more of: (i) soaking in an alkaline solution, e.g. sodium metasilicate, sodium tripolyphosphate, sodium carbonate, sodium hydroxide or the like, e.g. for a period of from 2 to 15 minutes; (ii) pickling in acid, e.g.
10 hydrochloric etc., e.g. for a period of 2 to 15 minutes; (iii) mechanical surface treatment, e.g. surface grinding, abrading or blasting using shot, sand or the like; and (iv) washing in water and/or organic solvent.

The present invention unexpectedly and beneficially
15 allows metallic materials comprising magnesium and its alloys to be produced which have superior properties compared with those produced by prior art processes as described earlier. In particular, the treatment provided by the invention gives magnesium based metallic
20 materials having a surface layer having suitable resistance to galvanic corrosion when in contact with other metallic materials. Such improved corrosion resistance may beneficially be obtained together with suitable surface electrical conductivity and mechanical
25 properties similar to or in some cases even higher than those of the untreated magnesium material.

The present invention therefore allows magnesium
based materials and articles made from such materials to be produced which are superior to comparable magnesium
30 based materials and products of the prior art.

Illustrative embodiments of the present invention will now be described with reference to the accompanying drawings in which:

Brief Description of the Drawings

5 Figure 1 is a process flow sheet of an example of the method according to the invention.

Figure 2 is a graph of corrosion potential versus diffused zinc content for a magnesium alloy treated by a method embodying the invention.

10 Figure 3 is a graph of Vickers micro-hardness measured at 50 grams load versus zinc content in the surface layer of magnesium alloy material treated in accordance with an embodiment of the invention.

Description of specific embodiments of the invention

15 Figure 1 is a flowsheet showing the steps involved in carrying out an example of the method according to a second aspect of the invention. A pre-cleaning or surface preparation step 1 is often required and carried out prior to treatment by a zinc
20 diffusion process 2. The pre-cleaning step 1 may comprise one or more of an alkaline soak 1a, acid pickling 1b and mechanical cleaning 1c. The pre-cleaning step 1 may also include washing (not shown in Figure 1) with water and/or organic solvent(s).
25 The standard of pre-cleaning prior to the zinc diffusion process 2 has an important influence on the corrosion protection which will be afforded to the treated material. This step 1 is important to free the surface of the material from heat treatment
30 scale, grease, other surface contaminations, mill

scale etc,. Three standard pre-cleaning methods are available and are shown in Figure 1 for use in the step 1. The material treated by each method must be carefully examined prior to the zinc diffusion
5 process 2, in order to ensure that the quality of the material has not been impaired by the pre-cleaning step. For example, where the material to be treated comprises a part which has been pre-formed in the shape of an article which has screw threads, it is
10 important to check that damage to the threads has not occurred, particularly where mechanical cleaning such as using a sand or shot blasting operation or grinding has been employed.

If the material to be treated is already in a
15 suitably clean condition (free of grease etc., as described earlier) it is possible to go directly to the zinc diffusion process 2 without pre-cleaning.

After the magnesium alloy material to be treated has been pre-cleaned to a satisfactory standard the
20 material is placed into a container. In practice, a plurality of pre-formed parts of the magnesium alloy material may be treated together. Zinc powder/dust is added, the quantity being determined by the surface area of the magnesium alloy parts to be treated. An
25 inert filler may or may not be added. The main purposes of the inert filler are to prevent damage to the treated magnesium alloy parts during operation and also to ensure even distribution of the zinc. The container is then closed, sealed, and placed inside a
30 furnace. The container may remain either stationary or be slowly rotated in the furnace. If the zinc

diffusion process is performed under air, then at this stage the temperature is raised to a predetermined level under accurate control. If the process is to be carried out under an inert gas atmosphere, or a reducing gas atmosphere, or a mixture of inert and reducing gases, then the gases are introduced into the furnace prior to raising the temperature.

The temperature at which the zinc diffusion process is carried out is in the range specified earlier which is thereby selected not to be sufficiently high as to affect the physical properties of the base magnesium alloy material being treated.

When the furnace operation is complete the sealed container is cooled. Then the treated magnesium alloy parts are removed from the container and are screened and cleaned to remove residual zinc dust and inert filler. The remaining zinc powder and (if employed) inert filler after the removal of the magnesium alloy parts may be discarded or preferably recycled and later re-used.

A specific example of the method illustrated in Figure 1 and a treated magnesium alloy product made using it will be described in Example 1 as follows.

Example 1

A casting was made of the magnesium alloy AZ91D. This was found using EDS to contain the following component elements: aluminium 9.3 ± 0.2 weight percent; zinc 0.6 ± 0.02 weight percent; and

manganese 0.29 ± 0.02 weight percent; the balance being magnesium. This material was found against a standard calomel electrode to have a corrosion potential of -1.71 volts.

- 5 The casting was surface treated using grinding on SiC (silicon carbide) paper with tap water to remove a surface rough layer about ~ 600 MESH (~20 μ m) thick, followed cleaning the resulting smooth surface with distilled water plus acetone plus alcohol and
10 then drying in air, and, after surface preparation and cleaning, was placed into a container together with zinc powder. The zinc powder was 99% pure zinc powder spheres having a mean diameter of 100 mesh (approx. 150 μ m) in an amount sufficient to cover the
15 surface of the casting (approximately 10 times the weight of the casting). The container was sealed and placed in a furnace having an accurate temperature control. The container was heated at a temperature of 330°C for a period of about 15 hours in the furnace.
- 20 When the heating step was completed, the container was removed from the furnace and cooled. The treated casting was removed from the container. The treated casting was found to show a corrosion potential of -0.361 volts as measured against a
25 standard calomel electrode. Such a low corrosion potential allows the material to be suitable for contact with many common metallic materials particularly those used in the electronics industry, e.g. stainless steel, phosphor bronze, nickel-chrome
30 alloy, tin-lead solder, etc. which all have a

corrosion potentials of between -0.2 volts and -0.5 volts.

The relationship between galvanic corrosion potential and percentage by weight of zinc diffused into the casting in the above Example 1 is shown in Figure 1 and is seen to be a roughly linear relationship. A minimum corrosion potential was obtained for a maximum zinc concentration in the surface layer of the treated material of about 6.8% by weight.

The treated casting produced in Example 1 was found to have a surface electrical conductivity which was similar to that of the untreated alloy casting. Also, the the microstructure (grain size and morphology) of the resulting treated material was compared by SEM (scanning electron microscope) and OM (optical microscope) with that of the untreated alloy casting and the two microstructures were found to be very similar, giving similar mechanical properties. Thus, the poor adhesion problem experienced with prior art coated materials described earlier was not evident.

Figure 3 is a graph of Vickers micro-hardness (measured in a standard way) for a load of 50 grams versus zinc content in the surface layer of the treated material. The change in Vickers micro-hardness resulting from the zinc diffusion treatment as compared to the untreated AZ91D magnesium alloy 'Base Material' is illustrated. As seen in Figure 3, the Vickers micro-hardness actually increases with added zinc content.

CLAIMS

1. A metallic material which comprises magnesium having a surface layer in which zinc has been diffused
5 into the material to provide atomic substitution of the magnesium, the material having a corrosion potential having a magnitude of less than -0.6 volts.
2. A material according to claim 1 and wherein the magnitude of the corrosion potential of the metallic
10 material is less than -0.5 volts
3. A metallic material according to claim 1 or claim 2 and which is a magnesium alloy containing at least 85% by weight magnesium.
4. A metallic material according to claim 3 and
15 wherein the alloy contains up to 12% by weight of aluminium.
5. A metallic material according to claim 3 or claim 4 and wherein the alloy contains other than in the surface layer up to 2% by weight of zinc.
- 20 6. A metallic material according to claim 3, claim 4 or claim 5 and wherein the alloy contains up to 0.5% by weight of manganese.
7. A metallic material according to any one of the preceding claims and wherein the surface layer of the
25 metallic material has a thickness of between 1 μ m and 7 μ m.
8. A metallic material according to any one of the preceding claims and wherein the concentration of zinc is at least five times greater, measured as a
30 percentage of overall weight of the material, in the said surface layer than in the interior of the metallic material.

9. A metallic material according to any one of the preceding claims and wherein the concentration of zinc in the surface layer is at least 5 per cent by weight.

10. A metallic material according to any one of the preceding claims and wherein the metallic material has the following further properties:

(ii) an electrical conductivity in its zinc diffused layer of at least 7.3 MS/m

(iii) a Vickers micro-hardness of at least 120 kg/mm² at 50 grams load.

11. A metallic material according to any one of the preceding claims and wherein the material has been cast and/or mechanically shaped by hot or cold metal working process.

12. A metallic material according to any one of the preceding claims and wherein the material is in the shape of an article.

13. A method of producing a metallic material according to any one of the preceding claims which method comprises heating a metallic material comprising magnesium together with zinc particles so that zinc diffuses into said material and produces a surface layer in which magnesium atoms are substituted by zinc.

14. A method according to claim 13 and wherein the zinc is substantially in elemental form and has a purity of at least 98% by weight.

15. A method according to claim 13 and wherein the zinc is in the form of a zinc compound or alloy.

16. A method according to claim 15 and wherein the zinc compound or alloy contains at least 50% by weight zinc.

17. A method according to claim 15 or claim 16 and wherein the zinc is in the form of an alloy with aluminium and/or magnesium.
18. A method according to any one of claims 13 to 17
5 and wherein the heating is carried out at a temperature of from 310°C to 350°C.
19. A method according to claim 14 and wherein the heating at the said temperature is carried out for a period of at least 4 hours.
- 10 20. A method according to claim 14 and wherein the ratio of the weight of zinc present to treat the metallic material to the weight of metallic material to be treated is in the range of from 6:1 to 12:1.
21. A method according to any one of claims 13 to 20
15 and wherein the zinc employed is in the form of particles or flakes having a mean size of less than 1000µm.
22. A method according to any one of claims 13 to 21 and wherein an inert filler is mixed with the zinc, the
20 inert filler forming up to 30% by weight based on the weight of zinc present.
23. A method according to claim 22 and wherein the inert filler is selected from kaolin, calcium carbonate, magnesium carbonate, talc, alumina, silica, mica
- 25 24. A method according to claim 22 or claim 23 and wherein the inert filler is a particulate material having a mean particle size of less than 200 µm.
25. A method according to any one of claims 13 to 24 and wherein the metallic material being treated and the
30 zinc and optionally any inert filler are contained in a sealed container which is heated in an oven or furnace in an atmosphere of air or inert or reducing gas or a

mixture thereof whilst remaining stationary or being slowly rotated.

26. A method according to any one of claims 13 to 25 and wherein the metallic material being treated has been
5 pre-formed by casting or other metal working process.

27. A method according to claim 26 and wherein the pre-formed material is in the form of one or more shaped articles.

28. A method according to any one of claims 13 to 27
10 and wherein prior to the heating the metallic material is subjected to a surface cleaning process.

29. A method according to claim 28 and wherein the surface cleaning process comprises one or more of (i) soaking in alkali; (ii) soaking in acid; (iii)
15 mechanical surface treatment and (iv) washing in water and/or organic solvent.

30. A method according to claim 13 and substantially as described herein with reference to Figure 1 of the accompanying drawings.



INVESTOR IN PEOPLE

Application No: GB 0115396.4
Claims searched: 1-30

Examiner: Matthew Lawson
Date of search: 11 January 2002

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.T): C7F

Int Cl (Ed.7): C23C

Other: Online: PAJ, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
Y	GB 412989 (DRUMM) - the whole specification.	1-29
Y	GB 261502 (NORTH) - the whole specification.	1-29
X	EP 0834592 A1 ✓ (TOYATA) - page 2 lines 51-57, page 3 lines 35-36 & 40-41, page 5 lines 22-24 & 33-34 and page 7 line 4.	1,2,7-19, 21,22,26-29
X	JP 2000160320 A ✓ (SHARP) - WPI Abstract Accession No. 00-447067/39, the PAJ abstract and figure 3.	1-12
X	US 4838063 ✓ (NISHITAMA) - column 3 lines 14-16 & 27-38 & 39-66 and column 6 lines 14-18.	1-29

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

